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Analysis of ionicity parameters using modified Penn energy gap model

B P Singh* and A K Ojha

Department of Physics, Institute of Basic Sciences,
Khandari, Agra-282 002, Uttar Pradesh, India

E-mail : bhanuprakashsingh@yahoo.com

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Abstract The Phillips Van-Vechten calculations of ionicity parameters based on the original Penn gap model are revised using the modified form due to Grimes and Cowley [*Canad. J. Phys.* **53** 2549 (1975)] The modified model used in the present study, is free from several approximations and is based on a more accurate numerical evaluation of the dielectric function the revised values of ionicity parameters are found to deviate significantly from the original estimates made by Phillips and Van-Vechten. The revised values of ionicity parameters are shown to make a clearcut distinction between four fold and six-fold coordinated structures and also to correlate very well with the interatomic force constants and the effective charge parameters in case of I-VII, II-VI and III-V crystals

Keywords Ionicity parameters, energy gap model, interatomic force constants

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The microscopic dielectric function of a solid plays the central role in the calculation of any property of the solid influenced by the screening effects of the valence and conduction electrons. Only for a small number of semiconductors, detailed calculations have been made [1] by incorporating explicit knowledge of band structure of the particular material. In the absence of such knowledge, Penn [2] derived a set of formulae based on an isotropic, nearly free electron model for the energy bands. The work of Penn was extended by Srinivasan [3]. However, the model adopted by Penn as well as by Srinivasan was so complicated that the dielectric function could not be evaluated analytically. They obtained approximate analytic expressions for the dielectric function after introducing several simplifications. Specifically, the square matrix elements were replaced by interpolation formula chosen to reproduce the zero and long wave vector values, and energies near the zone boundary were replaced by constant values rather than the exact expressions. Grimes and Cowley [4] have rectified these shortcomings by evaluating the sum directly as integrals over the spherical Brillouin zone. Results thus obtained are sufficiently accurate at small, intermediate and large wave vectors. The modified expression for the energy gap between bonding and antibonding states obtained by Grimes and Cowley [4] is physically more plausible and consistent with experimental data and with pseudo potential calculations [1, 5].

* Corresponding Author

Phillips [6] and Van-Vechten [7] have developed a comprehensive theory of ionicity of chemical bonding in binary crystals using the unrevised energy gap expression originally due to Penn [2]. In view of the modifications [4] discussed above, it becomes desirable to revise the calculations of Phillips and Van-Vechten for ionicity parameters. The studies of energy gap model and ionicity parameters have been the subject of current interest [8-12]. In the present study, we use the modified energy gap expression as derived by Grimes and Cowley in order to revise the estimates of ionicity parameters due to Phillips and Van-Vechten. The revised values of ionicity parameters *viz.* the ionic (heteropolar) and covalent (homopolar) contributions to the energy gap are used to explain the distinction between four-fold and six-fold coordinated crystal structures.

The modified expression for the energy gap between bonding and antibonding states evaluated numerically have been found to be [4]

$$\varepsilon_\infty - 1 = \left(\frac{\hbar\omega_p}{E_g}\right)^2 S_0 , \qquad (1)$$

where ε_∞ is the electronic dielectric constant, E_g is the average energy gap between bonding and ω_p antibonding states and ω_p is the plasma frequency given by

$$\omega_p^2 = \frac{4\pi Ne^2}{m} \tag{2}$$

Here, e and m are the electronic charge and mass respectively. N is the number of valence electrons per unit volume. In the original Penn model, the factor S_0 is nearly equal to unity. However, more accurate calculations performed by Grimes and Cowley reveal that $S_0 = 0.62$. This value of S_0 modifies the earlier estimates of ionicity parameters [6, 7] quite significantly.

The energy gap E_g can be split into an ionic (heteropolar) part C and covalent (homopolar) part E_h such that [6]

$$E_g^2 = E_h^2 + C^2. \tag{3}$$

The homopolar part E_h depends on the nearest neighbour separation R as follows

$$E_h = AR^{-k}, \tag{4}$$

where A and k are the constants, *i.e.* remain unchanged in different crystals. Values of E_g can be calculated with the help of eqs. (1) and (2) using experimental data on dielectric constants ε_∞ and unit cell volumes. The parameters A and k are then evaluated by applying eqs. (3) and (4) to purely covalent crystals *viz.* diamond and silicon which have $C = 0$ and therefore $E_g = E_h$. After knowing A and k in this manner, one can calculate E_h from eq. (4) by taking appropriate values of R for other solids. Values of E_g determined from eq. (4) enable us to obtain C with the help of eq (3). The ionicity of the chemical bond is defined in terms of fractional ionic character [6, 7] as given below

$$f_i = \frac{C^2}{E_g^2}. \tag{5}$$

The definitions and method of calculations as described above are due to Phillips and Van-Vechten. When we use eqs. (1) to (5) with $S_0 = 0.62$, we get $A = 54.0$ J and the exponent $k = 2.52$. The corresponding values obtained by Phillips and Van-Vechten were $A = 63.58$ J and $k = 2.48$. The revised values of E_g, E_h, C and f_i for sixty eight binary crystals are calculated using the input data on lattice parameters, unit cell volumes and electronic dielectric constants [8-16]. The results are given in Table 1.

It has been found [6] that the input data used in calculations are quite accurate and values of f_i can be calculated up to three digits after decimal. The present values of f_i do not differ much from the Phillips values of f_i in case of I-VII crystals such as alkali halides. However, the differences between the two sets of f_i become prominent in case of II-VI and III-V compounds. For example, in case of GaAs and GaSb, the values of f_i obtained in the present study are much lower than the corresponding values based on the Phillips ionicity scale. This would imply that such compounds have stronger covalent bond than that predicted by Phillips. It is worth mentioning here that the values of f_i predicted earlier by Pauling [17] using the thermochemical electronegativity data remain between 0.06 and 0.56 for III-V compounds. This is in close agreement with the range of f_i values for III-V compounds obtained in the present study. We have found that the revised values of f_i do not affect the correlation between f_i, interatomic force constants and effective charge parameters.

Table 1. Values of fractional ionic character f_i (a) Values calculated in the present study and (b) Values due to Phillips [6] and Van-Vechten [7, 8]

Crystals	f_i		Crystals	f_i	
	(a)	(b)		(a)	(b)
LiF	0.925	0.915	ZnSe	0.653	0.676
LiCl	0.915	0.903	ZnTe	0.637	0.546
LiBr	0.909	0.899	CdO	0.793	0.785
LiI	0.900	0.890	CdS	0.711	0.685
NaF	0.955	0.946	CdSe	0.635	0.699
NaCl	0.946	0.935	CdTe	0.615	0.675
NaBr	0.942	0.934	MgO	0.853	0.841
NaI	0.938	0.927	MgS	0.805	0.786
KF	0.962	0.953	MgSe	0.803	0.790
KCl	0.962	0.953	MgTe	0.653	0.554
KBr	0.960	0.952	CaO	0.872	0.913
KI	0.959	0.950	CaS	0.862	0.902
RbF	0.962	0.960	CaSe	0.850	0.900
RbCl	0.965	0.955	CaTe	0.833	0.894
RbBr	0.959	0.957	SrO	0.893	0.926
RbI	0.959	0.951	SrS	0.875	0.914
CsF	0.959	–	SrSe	0.872	0.917
CsCl	0.968	–	SrTe	0.856	0.903
CsBr	0.968	–	BaO	0.878	
CsI	0.969	–	BaS	0.886	–
CuF	0.781	0.766	BaSe	0.881	–
CuCl	0.762	0.746	BaTe	0.875	–
CuBr	0.738	0.735	AlN	0.451	0.449
CuI	0.676	0.692	AlP	0.327	0.307
AgF	0.899	0.894	AlAs	0.229	0.274
AgCl	0.879	0.856	AlSb	0.358	0.426
AgBr	0.861	0.850	GaN	0.469	0.500
AgI	0.754	0.770	GaP	0.333	0.374
BeO	0.632	0.602	GaAs	0.173	0.310
BeS	0.349	0.312	GaSb	0.066	0.261
BeSe	0.411	0.299	InN	0.507	0.578
BeTe	0.088	0.169	InP	0.341	0.421
ZnO	0.646	0.616	InAs	0.187	0.357
ZnS	0.644	0.623	InSb	0.079	0.321

The trends of variations of interatomic force constants [18] and effective charge parameters [19-21] with f_i remain similar to those predicted by Phillips [6].

The splitting of energy gap (E_g) into ionic (heteropolar) C and covalent (homopolar) E_h parts has been made in a symmetrical manner (equation 3) and it has ben found [6] that a plot of C *versus* E_h can provide a criterion for distinguishing between four-fold and six-fold coordinated structures. In Figure 1, we have plotted the revised values of C and E_h for all the sixty eight crystals under study. The plot makes a clear distinction between the four-fold and six-fold coordinated structures. The critical value of ionicity f_i is equal to 0.786 which separates the two regions unambiguously. It should be mentioned here that unrevised values of C and E_h reported by Phillips and Van-

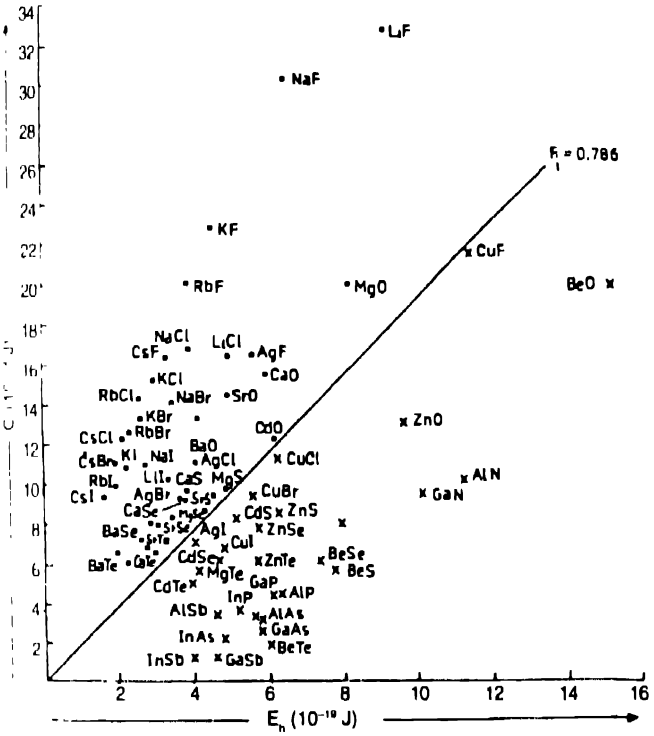

Figure 1. The separation of four-fold and six-fold coordinated structure using the plot between ionic part C and covalent part E_h

Vechten could not achieve such a clear cut distinction between the two types of structures. For example CdO, MgO and MgSe lie on the boundary line plot and hence, it was not possible to identify the structures for these compounds. On the other hand, the plot of C *versus* E_h based on the results obtained in the present study (Figure 1) makes the clear separation between the two types of crystal structures.

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